# PATENT SPECIFICATION

DRAWINGS ATTACHED

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**829,844**

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COMPLETE SPECIFICATION

## Production of Sulfur-Free Carbon Monoxide-Containing Gas

We, TEXACO DEVELOPMENT CORPORATION, a corporation organised under the laws of the State of Delaware, United States of America, of 135, East 42nd Street, New York 17, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of carbon monoxide-containing gas substantially free from sulfur-containing gases by the gasification of a sulfur-containing solid carbonaceous fuel.

The gasification of a solid carbonaceous fuel such as coal by reaction with a limited quantity of free oxygen to produce carbon monoxide may be carried out successfully at temperatures above about 1,800° F. Generally, the reaction is most satisfactorily conducted at a temperature in the range of 2,200 to 3,200°F. While air may be used directly as the source of free oxygen for such gasification, it is generally desirable to employ oxygen-enriched air or substantially pure oxygen to reduce the quantity of nitrogen in the product gas.

The reaction of a carbonaceous fuel with uncombined or free oxygen is an exothermic reaction. Steam or carbon dioxide, both of which undergo endothermic reaction with carbon, may be employed as supplemental reactants to control such exothermic reaction and to produce additional amounts of carbon monoxide and hydrogen.

The product gas from the gasification reaction comprises mainly carbon monoxide together with some carbon dioxide and hydrogen. Hydrogen is produced from hydrocarbon constituents of the fuel, from moisture contained in the fuel, or from steam supplied to the reactor. Nitrogen, which may be contained in either or both the fuel and the free oxygen-containing gas, usually appears also in the product gas stream. Many solid fuels contain sulfur. When such a sulfur-containing fuel is so reacted with free oxygen, a sulfur-containing gas, usually sulfur dioxide, is produced which is present in the product gas stream.

We have found that the quantity of such sulfur-containing gas appearing in the product gas stream may be reduced by the addition of lime to the gas generator or reactor. Lime ($CaO$), hydrated lime ($Ca(OH)_2$), or limestone ($CaCO_3$) is supplied to the gas generator by addition to the fuel. The amount of lime (calcium oxide or its equivalent as calcium hydroxide or calcium carbonate) required to remove the sulfur from the fuel is relatively small. Theoretically, each atom of calcium is capable of combining with an atom of sulfur contained in the fuel so that 1.75 pounds of calcium oxide are theoretically capable of removing 1 pound of sulfur from the fuel. In actual practice, we have found that more lime than the theoretical amount is required to remove all of the sulfur.

We have also found that, even when excess lime is added to the generator, some sulfur-containing gas still appears in the product gas stream. This is probably due to decomposition of the compound or compounds formed between the calcum and the sulfur at the temperatures existing in the generator.

In accordance with the present invention, the lime is supplied to the generator in an amount in excess of that theoretically required for the removal of all of the sulfur contained in the fuel. "Lime" is used in its broadest sense to include calcium oxide, calcium hydroxide and calcium carbonate. Calcium hydroxide or calcium carbonate so supplied to the gasification reaction zone is converted to calcium oxide at the reaction temperature. The product gas from the reactor is contacted with water containing lime (hydrated) either in solution or as a slurry. Substantially complete removal of the sulfur-containing gas is effected by such contact of the product gas with the limewater.

The present invention, therefore, provides a process for the production of carbon monoxide-containing gas substantially free from sulfur-containing gases from a sulfur-containing solid carbonaceous fuel also containing ash, which comprises reacting said fuel in admixture with lime in an amount in excess of that theoretically required for the removal of all the sulfur contained in the fuel with a free oxygen-containing gas in a reaction zone at a temperature above 2000°F. and also above the fusion point of the slag resulting from the lime and the ash from said fuel, contacting the resulting molten slag with water in a quench zone in the presence of the resulting carbon monoxide-containing product gas to effect solution of lime from said slag, withdrawing the product gas including a sulfur-containing gas from said quench zone, withdrawing limewater from said quench zone and effecting removal of a hydrogen sulfide-containing gas from the resulting limewater in the absence of said produce gas, and contacting said withdrawn product gas with said desulfurized limewater to effect removal of said sulfur-containing gas therefrom.

In carrying out the present invention, a solid carbonaceous fuel containing sulfur and an incombustible residue or ash is reacted in admixture with an appropriate amount of lime with a free oxygen-containing gas at a temperature above the fusion temperature of the ash or incombustible residue. The solid fuel may be gasified with fusion of the ash in a stationary bed (or downwardly moving bed) or in a flow-type reaction system. A flow-type gasification reaction system is defined as one in which pulverized solid fuel is reacted with free oxygen while in suspension in free oxygen-containing reactants and reaction products. In the flow-type generator, the solid and gaseous reactants are advantageously proportioned to produce substantially complete reaction of the fuel and free oxygen. Some excess fuel is usually supplied to the reactor, but this amount preferably is kept at a minimum. Preferably, relatively pure oxygen, for example, commercial oxygen containing above about 95 per cent oxygen by volume is employed as the free oxygen containing gas. Steam is preferred as a supplemental endothermic reactant. The ash is withdrawn from the gasification zone in molten form.

The lime added to the fuel reacts with the sulfur in the fuel and forms a slag with the incombustible residue from the fuel. Most coals may be fluxed with lime to yield a slag melting in the neighbourhood of 2,200°F. The quantity of lime required to produce the most fluid slag may be computed in accordance with conventional blast furnace practice. In general, the most fluid slag is obtained when the sum of the lime and any magnesia present is approximately equal in weight to the sum of the alumina and silica contained in the feed (fuel and flux). In some instances it may be desirable to add fluorspar, silica, alumina, magnesia, or recycle slag to the feed to the generator to increase the fluidity or quantity of the slag.

The accompanying drawing is a schematic flow diagram illustrating the principles of operation of the process of this invention. With reference to the drawing, a slurry of coal, water, and lime is prepared in a mixer 5. Part or all of the lime may be introduced into the system at this point or at a later point in the system, as will be brought out hereinafter. The slurry is picked up by pump 6 and passed through a tubular heater 7 at a velocity in excess of about 1 foot per second and sufficient to insure turbulent flow. The pump 6 increases the pressure on the slurry to an elevated pressure sufficiently in excess of the pressure in the gas generator 8 to produce flow through the heater. The water is vaporized from the slurry in the heater, forming a dispersion of solid particles in steam flowing at a velocity in excess of about 20 feet per second.

The particles of coal dispersed in steam and intimately associated with lime are introduced into the gas generator 8 into admixture with oxygen from line 9 in a suitable mixer-burner. If desired, steam may be separated from the dispersion in a suitable separator 11 which may be in the form of a cyclone-type separator. Steam and any other gases separated from the dispersion are discharged through line 12.

The generator comprises a compact, unpacked reaction zone autogenously maintained at a temperature in the range of 2,000 to 3,000° F. and also above the melting point of the slag resulting from the lime and the ash from the coal. With most U.S. bituminous coals, the slags have a melting point, when fluxed with lime, in the neighbourhood of 2,200°F.

The generator pressure may range from atmospheric to 2,000 pounds per square inch. Generally, a pressure above 100 psig and within the range of 100—400 psig is desirable.

The proportions of coal and free oxygen supplied to the generator are regulated to produce near-maximum amounts of carbon monoxide. Any steam supplied to the generator with the coal prevents excessive temperatures and, by reaction with carbon in the coal, serves as a source of hydrogen.

The product gas consisting principally of carbon monoxide and hydrogen is discharged from the generator 8 through an outlet 13 into a slag quench chamber 14. Molten slag drains from the generator into the slag quench chamber, which is desirably operated at substantially the same pressure. A quantity of water, the level of which is indicated by dotted line 16, is maintained in the quench chamber; the slag is dropped into the water and is immediately solidified and broken up into small discrete particles.

The product gas from the generator is with-

drawn through a transfer line 17 to a gas scrubber 18. Water from a suitable source, discussed in more detail hereinafter, is introduced through line 19 into transfer line 17 at the outlet from quench chamber 14 to quench the product gas stream.

Sulfur, introduced into the generator with the coal, reacts with the lime (and possibly with other constituents of the resulting slag) so that the slag from the generator contains sulfur, probably as calcium sulfide. Although calcium sulfide is decomposed by the water, some sulfur from the coal remains in the slag withdrawn from quench chamber 14 along with the resulting limewater through line 21 into flask tank 22.

Flask tank 22 is operated at substantially atmospheric pressure. Steam and other gases are liberated from the water-slag stream withdrawn from the quench chamber. Hydrogen sulfide is liberated with the steam, probably resulting from the hydrolysis of calcium sulfide to calcium sulfhydrate, $Ca(SH)_2 \cdot 6H_2O$, and decomposition of calcium sulfhydrate to calcium hydroxide and hydrogen sulfide. Stripping steam may be introduced into the flask tank through line 23.

The water and slag are drawn from flask tank 22 through line 24 into a settler 26. The settler may be provided with revolving arms 27. A settler of the type known as a Dorr thickener is suitable for use at this point in the process. The residual solid slag is withdrawn from the bottom of the settler while water containing dissolved constituents from the slag, principally lime, is withdrawn through line 28 to the top of gas scrubber 18. Lime may be added to the stream in line 28 from a hopper 29. Part or all of the lime required for the process may be supplied to the system at this point.

The limewater introduced into the top of scrubber 18 through line 28 flows downwardly through the scrubber where it contercurrently contacts the product gas stream from the generator introduced through line 17. Either a solution or a slurry of lime may be supplied to the scrubber through line 28. Preferably the gas scrubber is provided with a suitable arrangement of baffles or bubble cap trays to insure intimate contact between the gas and the limewater.

The product gas comprising carbon monoxide and hydrogen substantially free from sulfur-containing gases is discharged from the gas scrubber through line 31. Water is withdrawn from the bottom of scrubber 18 and passed through line 32 to stripper 33. Part of the water withdrawn from the bottom of gas scrubber 18 may be passed through line 34 into line 28 and recirculated to the top of the scrubber.

Stripper 33 is operated at a pressure lower than the pressure in the gas scrubber. The gas scrubber is usually operated at substantially the same pressure as the gas generator whereas the stripper 33 is preferably operated at substantially atmospheric pressure. Steam or carbon dioxide or both may be introduced through line 36 into stripper 33. Sulfur-containing gases associated with the water withdrawn from the gas scrubber through line 32 are eliminated from the water in stripper 33.

Carbon dioxide is preferred as the stripping agent in stripper 33. The carbon dioxide converts the calcium hydroxide contained in the water to calcium carbonate, which is only slightly soluble in water. The resulting slurry of calcium carbonate in water is passed through line 37 to a settling tank 38 where water substantially free from solid particles is decanted from the thickened slurry. The thickened slurry is passed through line 39 to mixing tank 5 where it is used in the preparation of the coal feed slurry for the generator. Part or all of the lime requirements may be supplied in the form of calcium carbonate from line 39.

Water separated from the slurry in settling tank 38 is passed through line 41 into quench chamber 14. Water from the same source may be passed through line 42 to line 19 to quench the product gas stream. Fresh water may be introduced, if desired, into line 19 from line 43 and may supply part or all of the water required for quenching the product gas. Water may be discarded from the system through line 44.

WHAT WE CLAIM IS:—

1. A process for the production of carbon monoxide-containing gas substantially free from sulfur-containing gases from a sulfur-containing solid carbonaceous fuel also containing ash, which comprises reacting said fuel in admixture with lime in an amount in excess of that theoretically required for the removal of all the sulfur contained in the fuel, with a free oxygen-containing gas in a reaction zone at a temperature above 2000°F. and also above the fusion point of the slag resulting from the lime and the ash from said fuel, contacting the resulting molten slag with water in a quench zone in the presence of the resulting carbon monoxide-containing product gas to effect solution of lime from said slag, withdrawing the product gas including a sulfur-containing gas from said quench zone, withdrawing lime water from said quench zone and effecting removal of a hydrogen sulfide-containing gas from this resulting limewater in the absence of said product gas, and contacting said withdrawn product gas with said desulfurized limewater to effect removal of said sulfur-containing gas therefrom.

2. A process according to claim 1, in which said reaction zone and said quench zone are each maintained at a pressure above 100 pounds per square inch gauge, and said withdrawn product gas is contacted with said desulfurized limewater at a pressure above 100 pounds per square inch gauge.

3. A process according to claim 2, in which the pressure on the resulting limewater is reduced to about atmospheric pressure in the absence of said product gas to thereby evolve said hydrogen sulfide-containing gas.

4. A process according to any of claims 1 to 3, in which the solution resulting from the contact of said withdrawn product gas with said desulfurized limewater is contacted with carbon dioxide to effect conversion of substantially all of the lime in said solution to calcium carbonate with simultaneous evolution of a sulfur-containing gas, and the calcium carbonate so obtained is supplied to said reaction zone as a source of said lime.

5. A process according to any of claims 1 to 3, in which particles of said fuel and lime are admixed with water to form a slurry; said slurry is passed as a continuous stream through a heating zone wherein the water is vaporized to form a dispersion of said particles of fuel and lime in steam; and said dispersion is introduced in admixture with said free oxygen-containing gas into said reaction zone.

6. A process according to claim 5, in which a sulfur-containing gas is stripped from the solution resulting from the contact of said withdrawn product gas with said desulfurized limewater, and the resulting stripped solution is supplied to the slurry preparation step.

7. A process for the production of carbon monoxide-containing gas substantially free from sulfur-containing gases from a sulfur-containing solid carbonaceous fuel also containing ash substantially as hereinbefore described.

8. Carbon monoxide-containing gas substantially free from sulfur-containing gases whenever produced by the process according to any of claims 1 to 7.

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829,844 COMPLETE SPECIFICATION

1 SHEET

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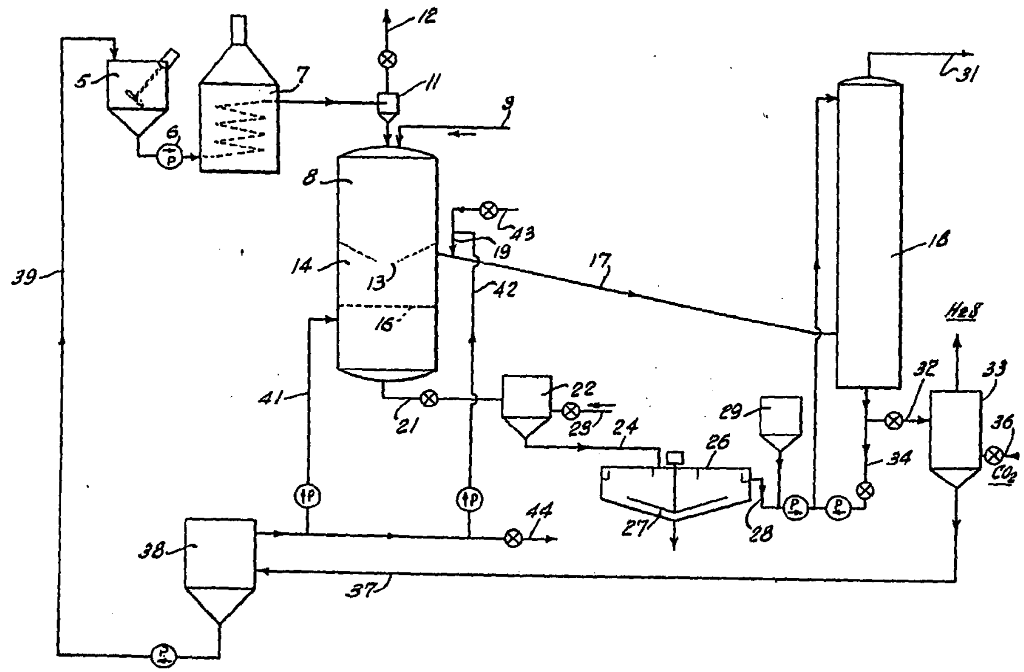

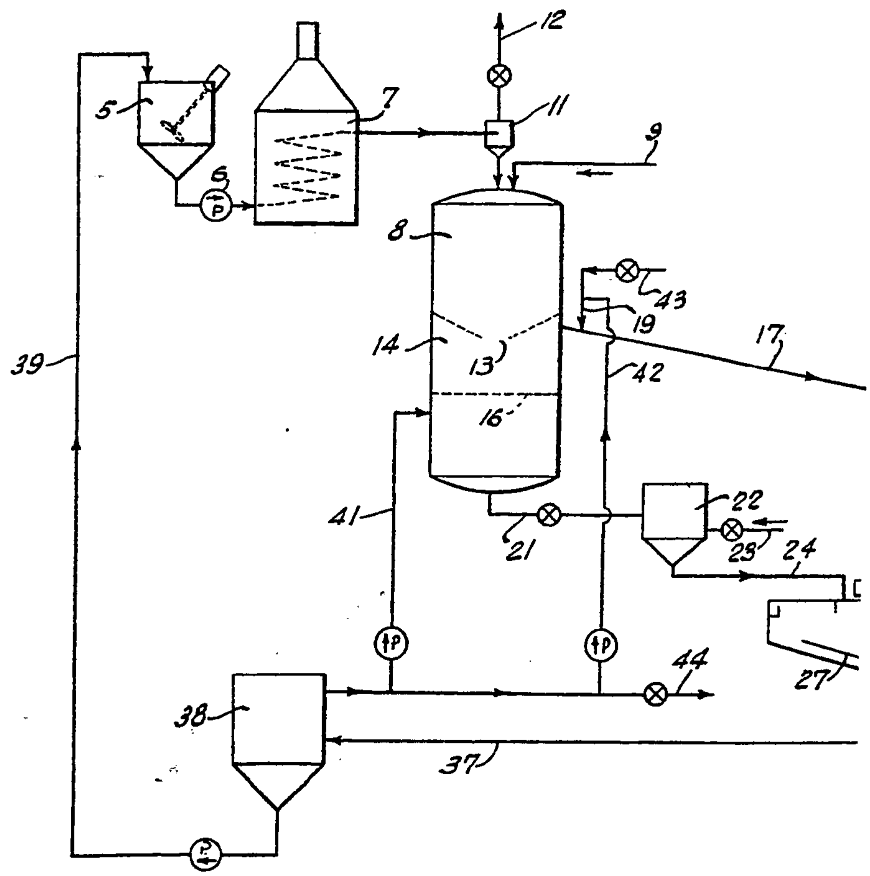

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829,844 COMPLETE SPECIFICATION
1 SHEET

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